CHAPTER VI

EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF ARSENIC

RESUME

The solvent extraction and spectrophotometric method for the determination of arsenic(III) is described. Arsenic forms a yellow coloured complex with N-p-tolyl-α-phenyl-p-methoxy-cinnamohydroxamic acid (PTPMCHA) at pH 4.5 - 5.2 which can be extracted into chloroform. The molar absorptivity of As-PTPMCHA is 1.3×10^4 l $mol^{-1}cm^{-1}$ at 410 nm. Many common ions associated with arsenic do not interfere. The effect of pH, reagent concentration and solvent is described. The arsenic is determined in standard samples.

INTRODUCTION

Arsenic and arsenical compounds are reported as waste products of the metallurgical glass, ceramic, dyes and pesticide industries. Insecticide industries discharge 362 mg/litre of arsenious oxide as waste products (1). Arsenic is a toxic element and can produce dermatitis, mild bronchitis and upper respiratory tract irritation. Maximum limits in whole blood and urinary levels are about 100 and 15 mg/litre respectively (2). According to an I.S.I. report the tolerance limit for arsenic for marine disposal is 0.2 mg/litre (3). Various reagents like halides, triphenylstanoammonium etc. were used for extraction and spectrophotometric determination of arsenic, but extraction is incomplete (4,5). Diethyl ammonium-dithiocarbamate was also used as an extracting reagent for arsenic (6,7) and Bi^{3+}, Pb^{2+}, Zr^{4+}, Th^{4+} and Ag^{+} are interfering. A preliminary distillation is also required prior to the extraction and moreover, diethylammonium diethyldithiocarbamate gets oxidised. Hydroxamic acids are potential analytical reagents used for the determination of several metal ions (8-10). With this view nine new hydroxamic acids have been synthesised and used for the extraction and spectrophotometric determination of arsenic in the present investigation.

EXPERIMENTAL

CHEMICALS AND REAGENTS

All the chemicals used were of AnalaR and GR grades of B.D.H. or E. Merck, unless otherwise specified.

Hydroxamic acids

These are synthesised as described in Chapter II. 0.05 M reagent solutions of hydroxamic acids were prepared in chloroform.

The standard arsenic solution (1 x 10^{-3} M) was prepared by dissolving requisite amount of arsenic trioxide into 250 ml of distilled water. The arsenic content was determined volumetrically (11).

APPARATUS

The spectral measurements were made on Shimadzu UV-VIS 240 spectrophotometer. The pH adjustments were made on Systronics digital pH meter, Model 324, equipped with glass and calomel electrodes.

A GBC 901 atomic absorption spectrophotometer equipped with a GBC HG 900 vapor generation assembly and arsenic hollow cathode lamp was used. The 193.7 nm, arsenic line and air acetylene flame were used for direct AAS measurements.

EXTRACTION PROCEDURE

Take 1 ml of arsenic solution (1.1 x 10^{-3} M) into 25-ml beaker, dilute to 10 ml with water and adjust pH 4.5 with buffer (acetic acid and sodium acetate). Transfer this solution into 100-ml separatory funnel. Add 10 ml of reagent solution, shake for 5 min and allow the phases to separate. Separate the yellow coloured chloroform layer and transfer into a 25-ml volumetric flask after drying over anhydrous sodium sulphate. Extract the aqueous layer with 5 ml of reagent solution to ensure the complete recovery of arsenic. Wash the anhydrous sodium sulphate with 2 ml of chloroform and finally dilute to 25 ml. Measure the absorbance at 410 nm against reagent as blank.

Atomic absorption measurements

The chloroform extract was directly aspirated into the flame for AAS measurements. However, for the lower concentration of arsenic (0.005 - 0.03 ppm) the arsenic was determined by the hydride method using GBC HG 900 vapor generation assembly. The following parameters were set for As: wavelength 193.7 nm, lamp current 8.0 mA, band pass 1.0 nm, working range 0.005-0.03 ppm of As, sample volume 20 ml, fuel air acetylene (flow rate 2.4 mm high), inert gas nitrogen at 20 psi.

The chloroform extract of As-PTPMCHA complex was back extracted with 10 ml of 6 M HCl and this acidic solution was used for determination of arsenic. The concentration of arsenic was computed from the calibration curve which was prepared in the range 0.005 - 0.03 ppm of As using the above method.

RESULTS AND DISCUSSION

The spectral characteristics of arsenic complexes with hydroxamic acid are summarised in Table 1. From the preliminary studies, it is observed that N-p-tolyl-α-phenyl-p-methoxy cinnamohydroxamic acid (PTPMCHA) is the most sensitive reagent amongst the hydroxamic acids studied here. Hence the optimum conditions for the extraction of arsenic with PTPMCHA have been further investigated.

Effect of pH

The As-PTPMCHA complex is extracted at the pH range 3-8 and the optimum pH for the extraction is pH 4.5-5.2. The data are summarised in Table 2.

Effect of solvents

As-PTPMCHA is extracted with various solvents viz. chloroform, carbon tetrachloride, iso-butyl methylketone and isoamyl alcohol etc. Chloroform is found the most suitable solvent for extraction of arsenic (Table 3).

Effect of reagent concentration

The extraction was carried out with various amounts of PTPMCHA in chloroform. It was observed that 10 ml of 0.05 M PTPMCHA in chloroform gives the complete extraction of arsenic (Table 4).

TABLE 1

Spectral characteristic of arsenic substituted cinnamohydroxamic acid complex

As(III) : 3.30 ppm
pH : 4.5
Hydroxamic acid: 0.05 M, 10 ml in $CHCl_3$
Solvent: $CHCl_3$
Shaking time : 5 min

Compd No.	Cinnamohydroxamic acid	λmax nm	Colour of complex	Molar absorptivity $l\ mol^{-1} cm^{-1}$	Sandell's sensitivity $\mu g\ cm^{-2}$
I	N-Phenyl-α-phenyl p-methoxy-	410	Yellow	1.1×10^4	0.0068
II	N-p-Tolyl-α-phenyl p-methoxy-	410	Yellow	1.3×10^4	0.0058
III	N-m-Tolyl-α-phenyl-p-methoxy-	410	Yellow	1.2×10^4	0.0062
IV	N-p-Chlorophenyl-α-phenyl-p-methoxy-	410	Yellow	1.0×10^4	0.0075
V	N-phenyl-α-phenyl-	410	Yellow	1.0×10^4	0.0075
VI	N-p-Tolyl-α-phenyl-	410	Yellow	1.1×10^4	0.0068
VII	N-m-Tolyl-α-phenyl-	410	Yellow	1.1×10^4	0.0058
VIII	N-p-Chlorophenyl-α-phenyl-	410	Yellow	9.8×10^3	0.0074
IX	N-Phenyl-α-phenyl-3,4,5 trimethoxy-	410	Yellow	1.0×10^4	0.0075

TABLE 2

Effect of pH on the extraction of arsenic

As(III) : 3.30 ppm
PTPMCHA : 0.05 M, 10 ml in $CHCl_3$
Shaking time : 5 min

Solvent : $CHCl_3$
λmax : 410 nm
Colour of complex : Yellow

pH	Absorbance	Molar absorptivity $l\ mol^{-1}cm^{-1}$	% E
3.0	0.40	9.0×10^3	69.0
4.0	0.49	1.1×10^4	84.5
4.2	0.54	1.2×10^4	93.1
4.5	0.58	1.3×10^4	100
4.7	0.58	1.3×10^4	100
5.0	0.58	1.3×10^4	100
5.2	0.58	1.3×10^4	100
5.5	0.54	1.2×10^4	93.1
6.0	0.45	1.0×10^4	77.6
7.0	0.38	8.5×10^4	65.5
8.0	0.31	7.0×10^4	53.4

TABLE 3

Effect of solvents on the extraction of arsenic

Arsenic(III) : 3.30 ppm

PTPMCHA : 0.05 M, 10 ml in $CHCl_3$

Shaking time : 5 min

pH : 4.5

λmax : 410

Colour of complex: Yellow

Solvents	Molar absorptivity l $mol^{-1}cm^{-1}$	% E
Chloroform	1.3×10^4	100.00
Carbon tetrachloride	1.0×10^4	77.00
Isobutylmethyl ketone	1.1×10^4	86.00
Isoamyl alcohol	8.9×10^3	68.50

TABLE 4

Effect of reagent concentration

Arsenic(III) : 3.30 ppm

PTPMCHA : 10 ml in $CHCl_3$

pH : 4.5

λmax : 410 nm

Colour of complex: Yellow

Concentration of PTPMCHA (M)	Absorbance	Molar Absorptivity l mol^{-1}cm^{-1}	% E
0.02	0.29	6.5×10^3	50.0
0.04	0.41	9.2×10^3	70.7
0.05	0.58	1.3×10^4	100.0
0.10	0.58	1.3×10^4	100.0
0.15	0.58	1.3×10^4	100.0

TABLE 5

Effect of cations and anions on the extraction of arsenic(III)

Arsenic(III) : 3.30 ppm
PTPMCHA : 0.05 M, 10 ml in $CHCl_3$
Shaking time : 5 min

pH : 4.5
Solvent : $CHCl_3$
λ max : 410 nm
Colour of complex: Yellow

Ions	Added as	Amount added (mg)	Absorbance
Ag^{1+}	$AgNO_3$	20	0.58
Sr^{2+}	$SrCl_2$	25	0.58
Ba^{2+}	$BaCl_2$	25	0.58
Cd^{2+}	$CdSO_4$	20	0.58
Cd^{2+}	$CaCl_2$	20	0.58
Cu^{2+*}	$CuSO_4$	25	0.57
Pb^{2+}	$Pb(NO_3)_2$	20	0.58
Mg^{2+}	$MgSO_4$	20	0.58
Fe^{3+*}	$FeCl_3$	20	0.59
Sn^{2+}	$SnCl_2$	20	0.57
Sb^{3+}	$K(SbO)CuH_4O_6 \cdot \frac{1}{2}H_2O$	20	0.58
Ti^{4+**}	TiO_2	20	0.58
Zr^{4+}	$ZrOCl_2$	15	0.58
Nb^{5+}	Nb_2O_5	25	0.58
V^{5+}	NH_4VO_3	30	0.57
Mo^{6+}	Na_2MoO_4	25	0.58
Al^{3+}	$Al(NO_3)_3$	20	0.58
Ni^{2+***}	$NiCl_2.6H_2O$	20	0.58
Pd^{2+}	$PdCl_2$	25	0.58
F^-	NaF	15	0.58
Br^-	NH_4Br	15	0.58
I^-	KI	15	0.58
SO_4^{2-}	Na_2SO_4	20	0.58

* Masked with ascorbic acid
** Masked with NaF
*** Masked with DMG

Beer's law

A yellow coloured As-PTPMCHA extract in chloroform obeys Beer's law in the range 0.33-8.0 ppm of arsenic. The molar absorptivity is 1.3×10^4 l $mol^{-1} cm^{-1}$ at 410 nm.

Effect of diverse ions

Different amounts of diverse ions were added to a fixed amount of arsenic and the arsenic was extracted according to the procedure. Most of the metal ions associated with arsenic do not interfere, except Cu^{2+}, Fe^{3+}, Ti^{4+}, and Ni^{2+}. The interference from large amounts of Cu^{2+}, Fe^{3+} can be tolerated by masking with ascorbic acid, Ti^{4+} with NaF and Ni^{2+} with dimethyl glyoxime (DMG). The data are given in Table 5.

Composition of the complex

The composition of the arsenic complex was studied by the slope ratio method (12). Arsenic forms 1:3 complex with PTPMCHA extractable into chloroform. The stoichiometry of As-PTPMCHA complex was determined by taking fixed amount of arsenic and gradually increasing the amount of the reagent (L_1). The slope of the plot of log D_M vs -log (L_1) was found 3.0, confirms the metal to ligand (PTPMCHA) ratio 1:3.

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